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## **Supporting Information**

## Shorter might be better: oligo(oxazoline)s for thermoresponsive polymersomes

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Figure S1. <sup>1</sup>H-NMR spectra of HDOT in CDCl<sub>3</sub>



Figure S2. <sup>13</sup>C-NMR spectra of HDOT in CDCl<sub>3</sub>



**Figure S3.** <sup>1</sup>H-NMR spectrum of di-phtalimidated co-oligomer in CDCl<sub>3</sub> with the corresponding calculation of DF (e.g. B3)



Figure S4. DOSY spectra of di-aminated homo-oligomers (oligoMeOx: A; oligoBuOx: B) and B2 (C) in CDCl<sub>3</sub>



Figure S5. SEC traces of oligo(oxazoline)s in DMF



**Figure S6.** MALDI-TOF mass spectrum of oligoMeOx, an expanded region of the spectrum (down) showing the m/z of repetitive MeOx unit, the calculated and the experimental values of molecular weight in the arbitrary case of  $DP_n=12$ .



**Figure S7.** MALDI-TOF mass spectrum oligoBuOx, an expanded region of the spectrum (down) showing the m/z of repetitive MeOx unit, the calculated and the experimental values of molecular weight in the arbitrary case of  $DP_n=12$ 



Figure S8. Formulation of B2 oligomer in PBS, at a concentration of 1 g/L, prepared by direct dissolution method: representative TEM images at different scales, respectively 2  $\mu$ m (A: 25 °C), 1  $\mu$ m (B: 25 °C, G: 50 °C) and 500 nm (C: 25 °C, H: 50 °C); particle size distributions by TEM (D: 25 °C, I: 50 °C); correlogram curves by DLS (E: 25 °C, J: 50 °C); particle size distributions by DLS (F: 25 °C, K: 50 °C); zoom region showing the tortuosity of polymersome membrane (L); TEM capture (1  $\mu$ m scale) of the sample cooled back from 50°C at 25°C (M).



Figure S9. Formulation of B3 oligomer in PBS, at a concentration of 1 g/L, prepared by direct dissolution method: representative TEM images at different scales, respectively 2  $\mu$ m (A: 25 °C, F: 50 °C), 1  $\mu$ m (B: 25 °C, G: 50 °C); particle size distributions by TEM (C: 25 °C, H: 50 °C); correlogram curves by DLS (D: 25°C, I: 50 °C); particle size distributions by DLS (E: 25 °C, J: 50 °C).



Figure S10. DSC thermograms (heating cycle, between 0-140  $^{0}$ C, 10  $^{0}$ C/min) of block oligomers (A); Evolution of melting temperature (T<sub>m</sub>) in block oligomers series (B).

\* Kohlan, T. B., Atespere, A. E., Yildiz, M., Menceloglu, Y. Z., Unal, S., Dizman, B., Synthesis and Structure–Property Relationship of Amphiphilic Poly(2-ethyl-co-2-(alkyl/aryl)-2-oxazoline) Copolymers. *ACS Omega.* **2022**, *7*, 40067-40077. doi: https://doi.org/10.1021/acsomega.2c04809.



50°C





25°C

В





25 °C



Figure S11. Representative TEM images of the formulations of S2 oligomer (A), RB2 oligomer (B) and CB2 oligomer (C) in PBS, at a concentration of 1 g/L, prepared by direct dissolution method, at 25 °C and at 50 °C, at 1  $\mu$ m magnification.



Figure S12. Formulation of RB2 oligomer in PBS, at a concentration of 1 g/L, prepared by film rehydration method: representative TEM images at different temperatures (25 °C, 1  $\mu$ m and 500 nm magnification, A-C) and (50 °C, 1  $\mu$ m magnification, G); particle size distributions by TEM (F: 25 °C).



**Figure S13.** Formulation of **B2** oligomer in PBS, at a concentration of 1 g/L, prepared by film rehydration method: representative TEM images at different temperatures (25 °C, 1  $\mu$ m magnification, A) and (50 °C, 1  $\mu$ m magnification, G); particle size distributions by TEM (B: 25 °C, H: 50 °C); correlogram curves by DLS (C: 25 °C, I: 50 °C); particle size distributions by DLS (D: 25 °C, J: 50 °C).



Figure S14. Thermal response of B3 in PBS solution (pH 7.4; concentration of 1 g/L), evaluated by DLS. Each measurement was done in triplicate. The measurements were recorded between 10-50 °C.



Figure S15. DLS traces RB1 and RB3 prepared by direct dissolution in PBS (pH 7.4; concentration of 1 g/L), at 25°C and 50 °C.